

Supplementary Data

Key Role of Entropy in Nanoparticle Dispersion: Polystyrene-nanoparticle / Linear-polystyrene Nanocomposites as A Model System

*José A. Pomposo**, *Alaitz Ruiz de Luzuriaga*, *Agustín Etxeberria* and *Javier Rodríguez*

Entropy Changes upon Mixing

We are interested in estimating the entropy change experienced by the pure components (polystyrene-nanoparticles and linear-polystyrene chains) upon mixing. By using a simple hard sphere fluid model (S1-S3), the entropy change for component 1 (polymer-nanoparticles), $(S_m^{(1)} - S_1)$, is given by

$$\nu_1(S_m^{(1)} - S_1)/Vk_B = -\phi_1 \left(\ln \phi_1 + \frac{4\phi_1 - 3\phi_1^2}{(1-\phi_1)^2} - 1 \right) - \phi_1 (\nu_1 s_1^{HS} / V_1 k_B) \quad (E1)$$

where ν_1 is the nanoparticle volume, V is the total system volume, k_B is Boltzmann constant, ϕ_1 is the volume fraction of nanoparticles in the mixture and s_1^{HS} / V_1 is the reference entropy for the pure fluid (per unit volume)

$$\nu_1 s_1^{HS} / V_1 k_B = -\phi_f \left(\ln \phi_f + \frac{4\phi_f - 3\phi_f^2}{(1-\phi_f)^2} - 1 \right) \quad (E2)$$

Note that the reference entropy corresponds to that of the fluid at maximum packaging volume fraction without freezing (S2, S3), $\phi_f = 0.494$, since we are dealing with the components in the disordered, molten state.

Concerning the linear-polymer chains, by taking into account the translational entropy and the stretching entropy changes one can write

$$\nu_1(S_m^{(2)} - S_2)/Vk_B = -t\phi_2 \left(\ln \phi_2 + \frac{3}{2} \left[\frac{R_g^2}{R_{g0}^2} - 1 \right] \right) \quad (E3)$$

where $t = \frac{V_1}{V_2}$ and ν_2 is the polymer chain volume, ϕ_2 is the volume fraction of polymer chains in the mixture, R_{g0}^2 is the mean squared gyration radius of the chains in the pure

component and R_g^2 is the mean squared gyration radius of the chains in the mixture.

According to recent neutron scattering experimental data (S4), for cross-linked polystyrene-nanoparticles dispersed in a linear-polystyrene matrix equation E3 becomes

$$v_1(S_m^{(2)} - S_2)/Vk_B \approx -t\phi_2 \left(\ln \phi_2 + \frac{3}{2} \left[(1 + \phi_1)^2 - 1 \right] \right) \quad (\text{E4})$$

Then, the neat change in entropy upon mixing polymer-nanoparticles and chemically similar linear-polymer chains, S , is then simply obtained as $S = (S_m^{(1)} - S_1) + (S_m^{(2)} - S_2)$.

Thermodynamic Parameters and Miscibility Boundary Predictions

Based on equation E1-E4 and assuming athermal mixing, the free energy of mixing, F , is just obtained from $F = -TS$. It is well known that for a binary blend to be thermodynamically stable against phase separation the following conditions must be fulfilled simultaneously: $F < 0$ and $F^{(2)} > 0$, being $F^{(2)} = \frac{\partial^2 F}{\partial \phi_1^2}$ the second derivative of the

free energy of mixing with composition (S5). $F^{(2)}$ is related to quantities that can be obtained from Small Angle Neutron Scattering (SANS) experiments (such as the Flory interaction parameter, χ). Additionally, the condition $F^{(2)} = 0$ just determines the spinodal miscibility boundary.

In terms of the present model, $F^{(2)}$ is given by

$$v_1 F^{(2)} / Vk_B T = \frac{1}{\phi_1} + \frac{t}{\phi_2} - 2 \left(\frac{3}{2} t (1 + 3\phi_1) - \frac{4 - \phi_1}{(1 - \phi_1)^4} \right) \quad (\text{E5})$$

To be consistent with SANS analysis procedures for binary polymer blends (S4), where the common reference volume is that of the polymer repeat unit denoted as v_0 , we rewrite equation E5 as

$$v_0 F^{(2)} / Vk_B T = \frac{1}{r\phi_1} + \frac{1}{N\phi_2} - 2 \left(\frac{3}{2} \frac{(1 + 3\phi_1)}{N} - \frac{4 - \phi_1}{r(1 - \phi_1)^4} \right) \quad (\text{E6})$$

being $r = \frac{v_1}{v_0}$ and $N = \frac{v_2}{v_0}$. By comparison of E6 with the standard treatment of binary

polymer blend miscibility in terms of the Flory-Huggins theory (S5) we have

$$\chi \equiv \left(\frac{3(1+3\phi_1)}{2N} - \frac{4-\phi_1}{r(1-\phi_1)^4} \right) \quad (\text{E7})$$

We have employed equation E7 to estimate the Flory χ interaction parameter for 211-kD tightly cross-linked polystyrene-nanoparticles (2 wt %, nanoparticle radius ~ 4 nm) dissolved in 473-kD linear-polystyrene (radius of gyration ~ 18 nm, $N = 4550$) (S4). The calculated value, $\chi_{cal} = -2.3 \times 10^{-3}$ is in very good agreement with that obtained from neutron scattering data ($\bar{\chi}_{exp} = -2 \times 10^{-3} \pm 1 \times 10^{-3}$) (S4).

Finally, the spinodal miscibility boundary is determined from

$$\frac{1}{r\phi_1} + \frac{1}{N\phi_2} - 2 \left(\frac{3(1+3\phi_1)}{2N} - \frac{4-\phi_1}{r(1-\phi_1)^4} \right) = 0 \quad (\text{E8})$$

For a given blend composition, equation E8 allows one to *predict* the miscibility boundary for cross-linked polystyrene-nanoparticles dissolved in a linear-polystyrene matrix as a function of nanoparticle radius, a ($a \propto r^{1/3}$) and polymer radius of gyration, R_g ($R_g \propto N^{1/2}$).

Supplementary References

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